Electronic Supplementary Information

Copper(II) and iron(III) complexes with arylhydrazone of ethyl 2-cyanoacetate or formazan ligands: *E/Z* isomerization assisted by cooperative coordination and ionic interaction, catalysts for oxidation of alcohols

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1. ^{1}H NMR spectra and ESI-MS analysis

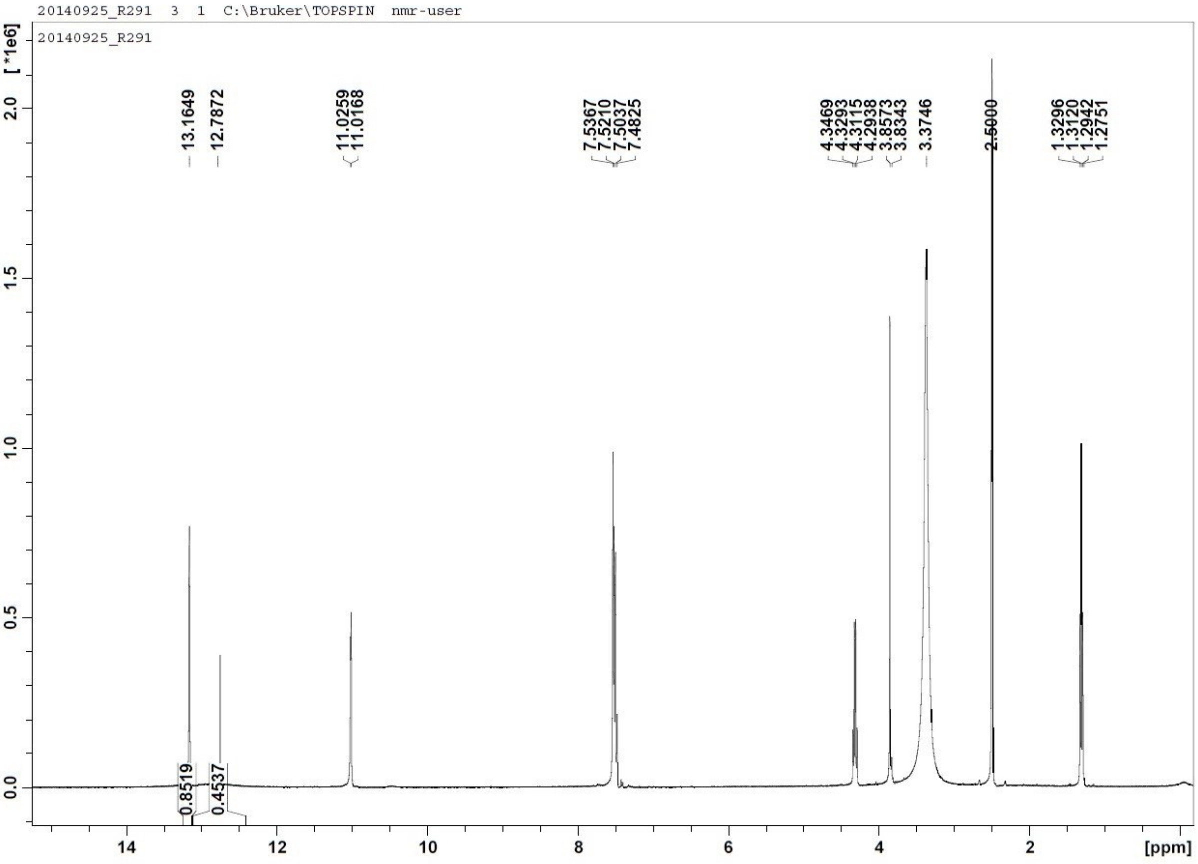


Figure S1. ^{1}H NMR spectrum of H_3L^1 in DMSO-d_6.

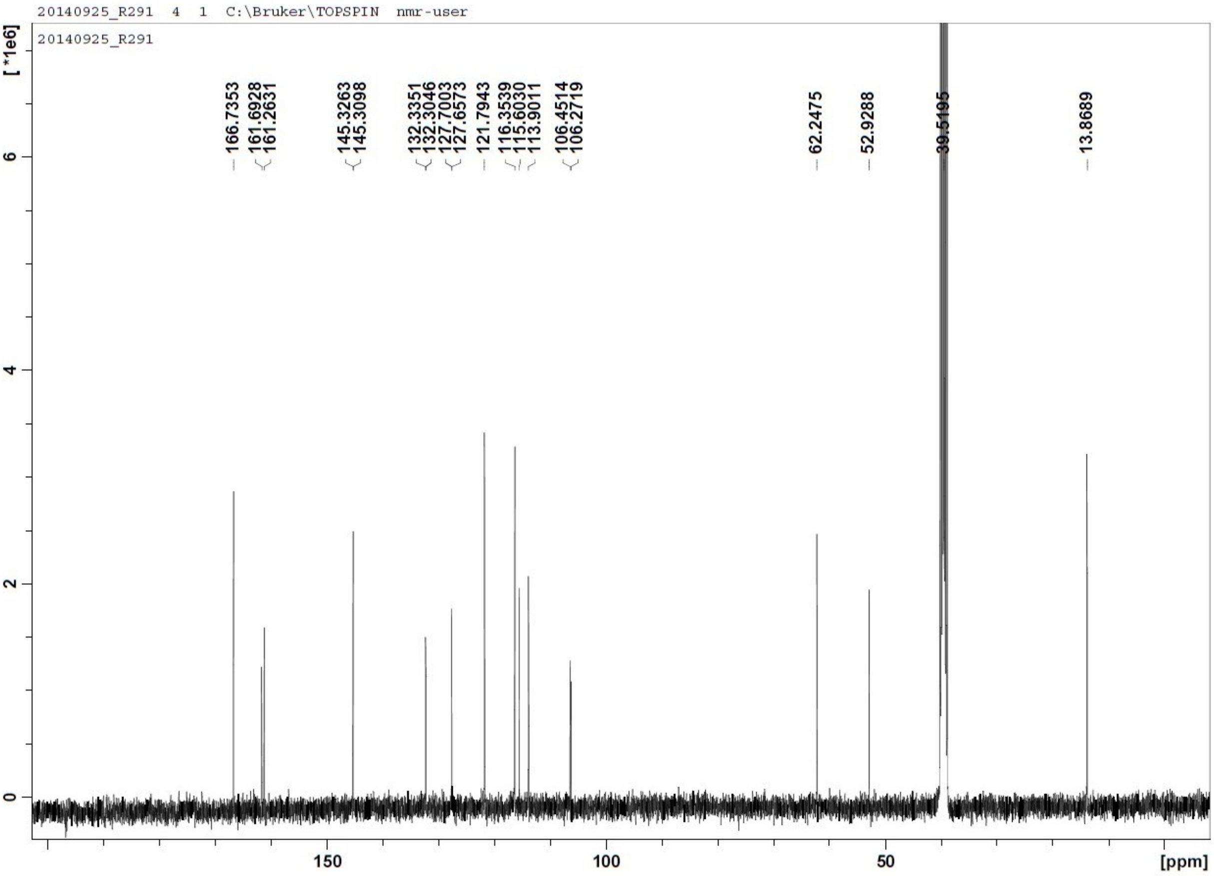


Figure S2. ^{13}C NMR spectrum of H_3L^1 in DMSO-d_6.

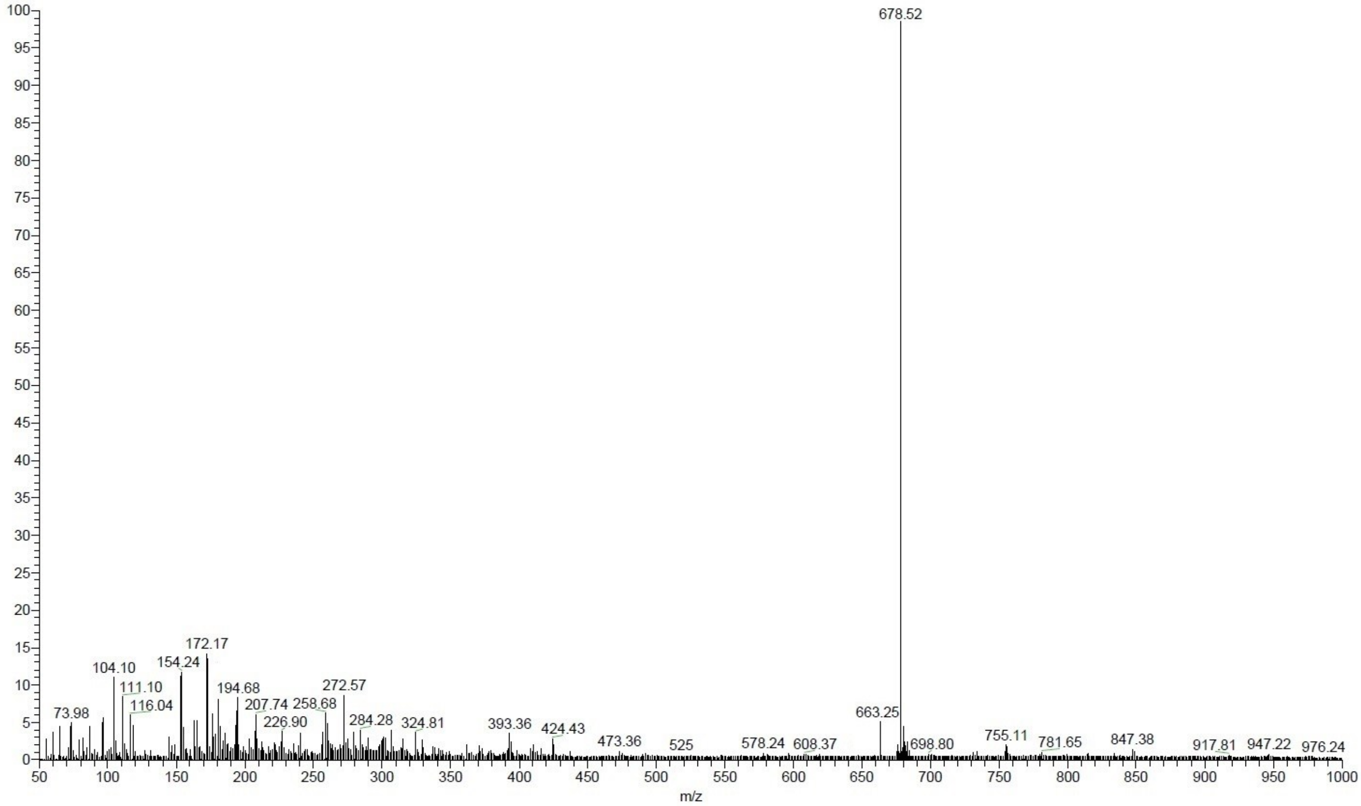


Figure S3. ESI-MS spectrum of **1**.

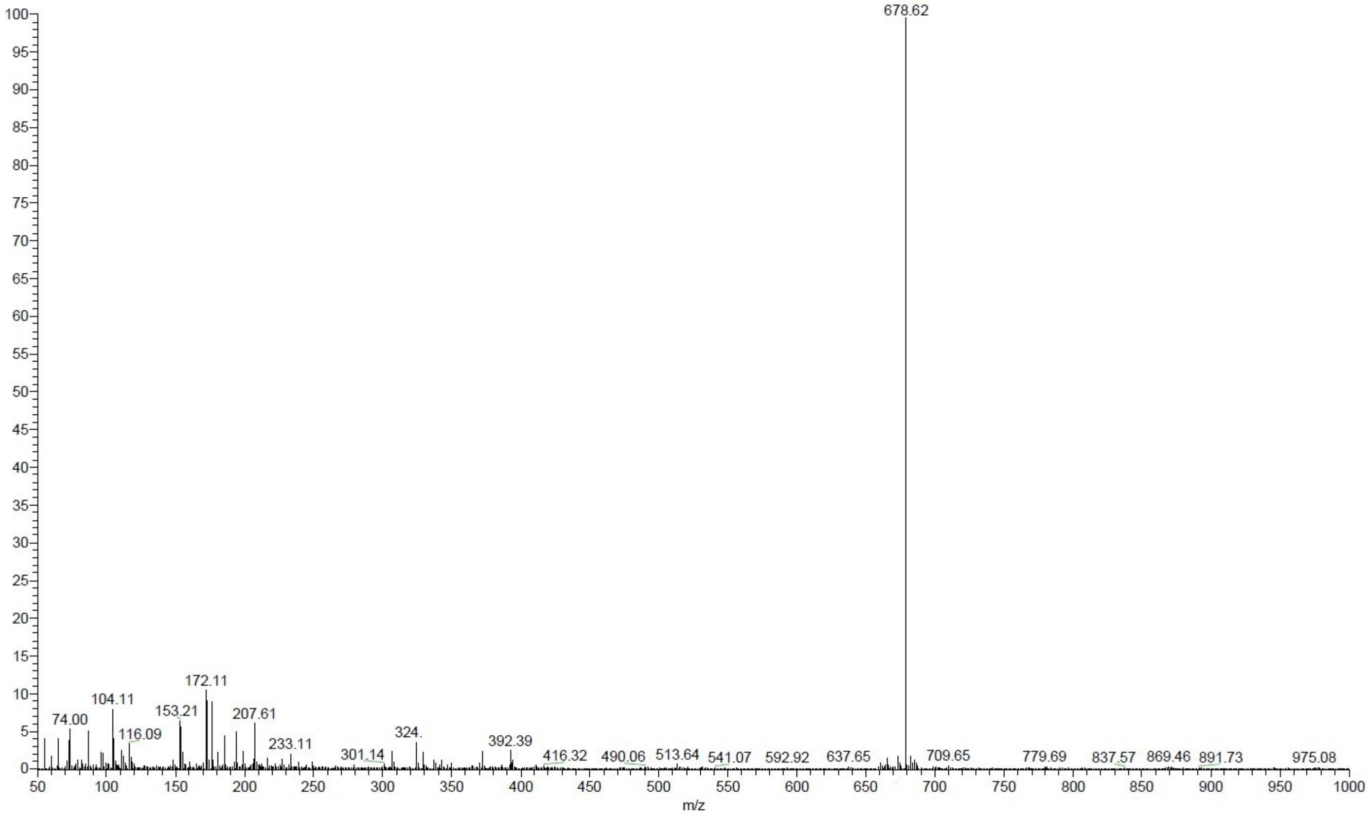


Figure S4. ESI-MS spectrum of **2**.

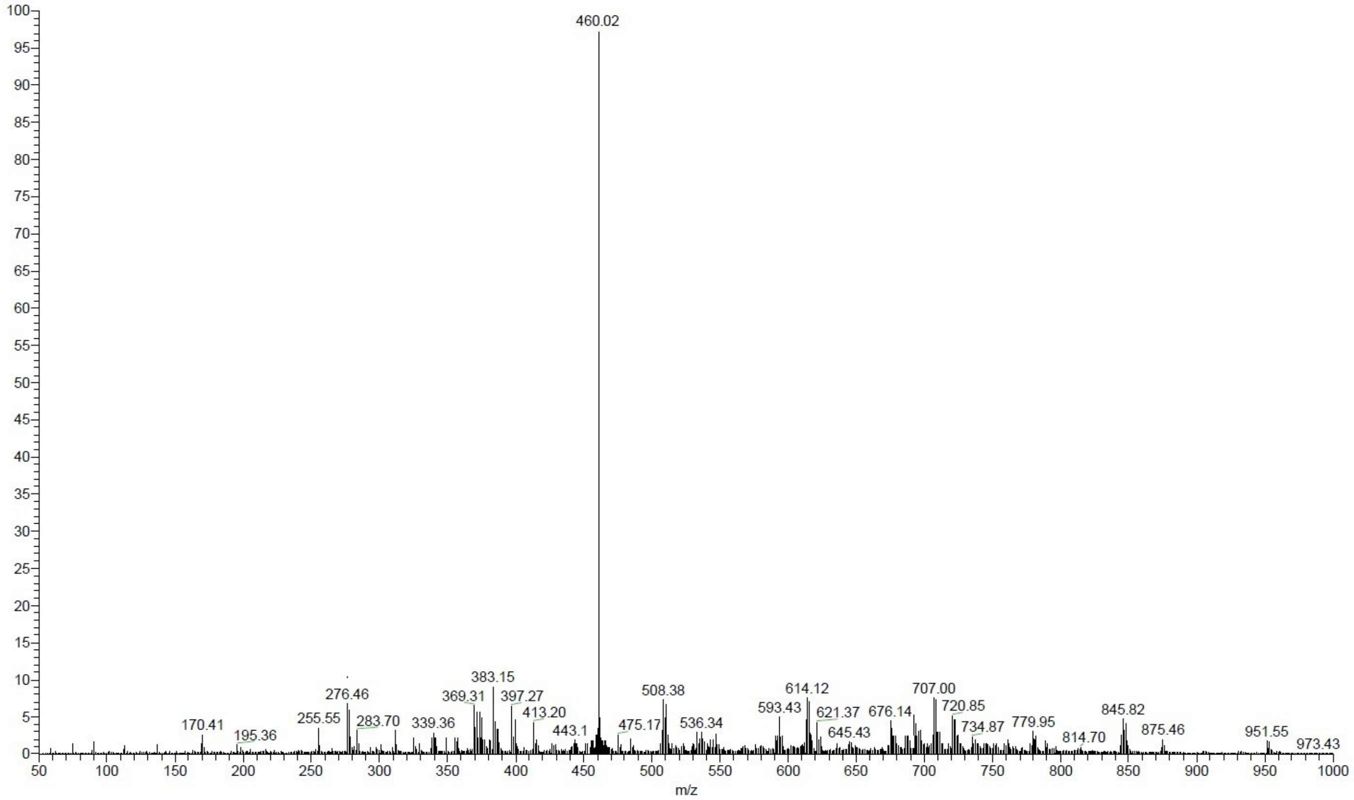


Figure S5. ESI-MS spectrum of **3**.

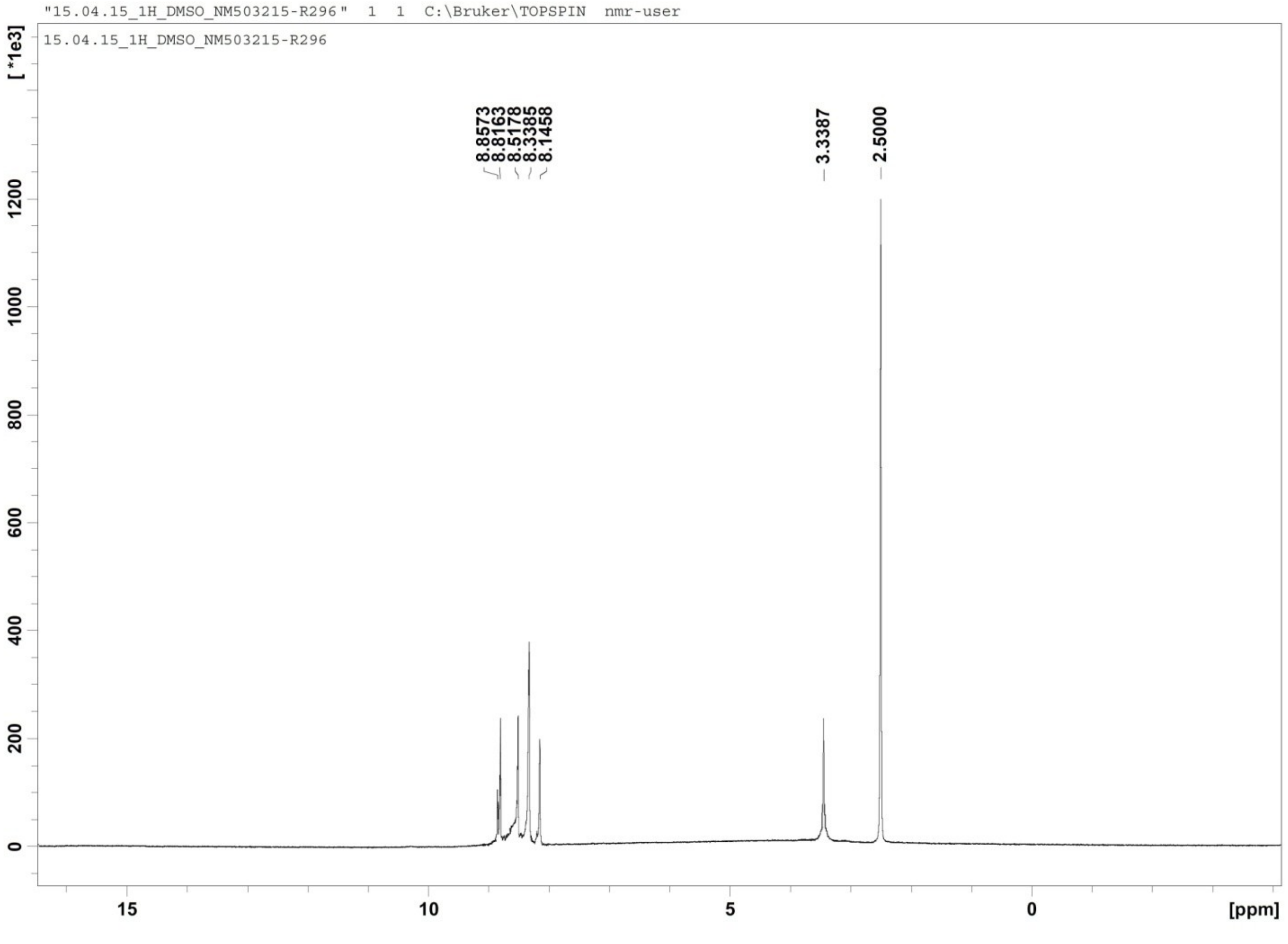


Figure S6. ^{1}H NMR spectrum of H_3L^2 in DMSO-d_6.

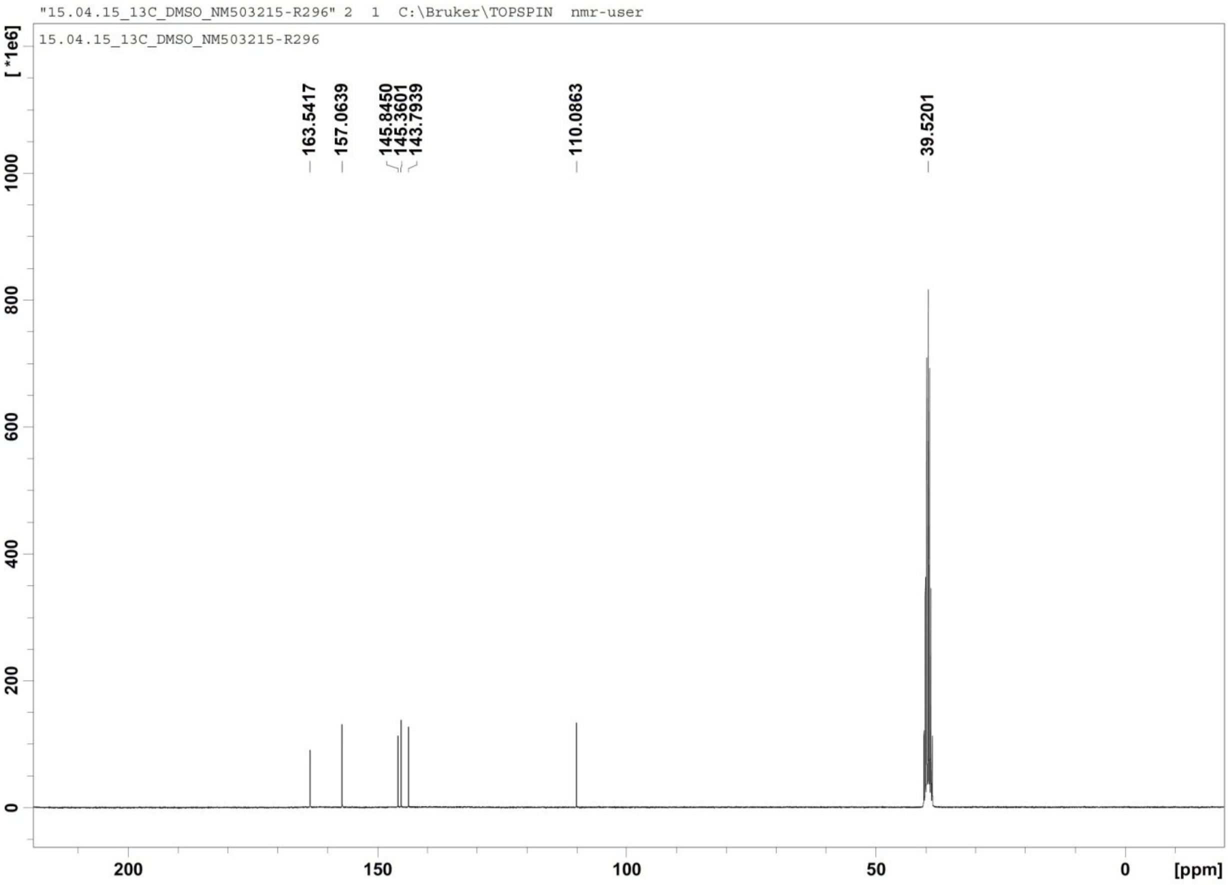


Figure S7. ^{13}C NMR spectrum of H_3L^2 in DMSO-d_6.

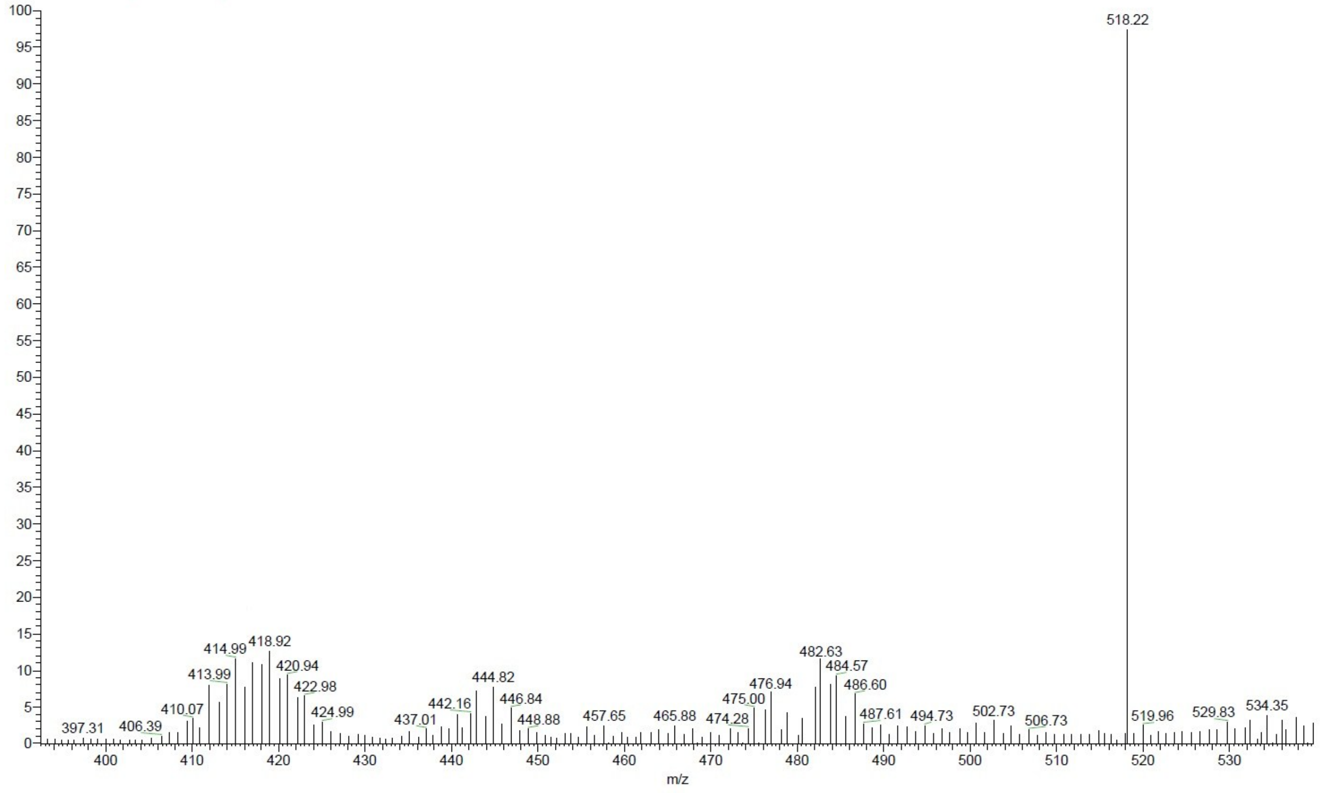


Figure S8. ESI-MS spectrum of **4**.

2. Evans NMR method

2.1. Evans NMR method calculation for effective magnetic moment [G. A. Bain, J. F. Berry, *J. Chem. Educ.* **2008**, *85*, 532-536].

$$\mu_{eff} = \sqrt{\frac{3\,k_{\mathrm{B}}}{N_A \beta^2}\left(\chi_M^P T\right)}$$

where k_B = Boltzmann constant; N_A = Avogadro's number; β = Bohr magneton; χ_P = molar susceptibility; T = absolute temperature (K).

2.2. Evans NMR method calculation for mass susceptibility [C. Piguet, *J. Chem. Educ.* **1997**, *74*, 815-816].

$$\chi = \frac{\delta v^p}{v_o S_f m^p} + \chi_o$$

where δv^p = Shift in frequency for an internal inert reference; *t*-butanol (Hz); v_o = frequency of the NMR spectrometer (Hz); S_f = Shape factor of the NMR spectrometer; 4π/3 sample axis parallel to magnetic field; m^p = concentration of solute (g/mL); χ_o = mass susceptibility of the deuterated solvent (mL/g).

2.3. Evans NMR method calculation for molar susceptibility [Piguet, C.; *J. Chem. Educ.* **1997**, *74*, 815-816]

$$\chi_M^P = \frac{\delta v^p M^p}{v_o S_f m^p} - \chi_M^{dia}$$

where δv^p = Shift in frequency for an internal inert reference; *t*-butanol (Hz); M^P = Molecular weight of solute (g/mol); v_o = frequency of the NMR spectrometer (Hz); S_f = Shape factor of the NMR spectrometer; 4π/3 sample axis parallel to magnetic field; m^p = concentration of solute (g/mL); χ_M^{dia} = diamagnetic constant (mL/mol).

Table S1. Evans NMR method data and parameters for complex **4**.

Mass (mg)	Volume (mL)	Molecular weight of solute (g/mol)	Concentration of solute (mol/L)	Deuterated Solvent	pD	Water Mass Susceptibility (mL/g)	Temperature (K)	Frequency of NMR spectrometer (Hz)	Shift in frequency (Hz)	Mass Susceptibility (mL/g)	Molar Susceptibility (mL/mol)	μ_{eff} (μ_β)
4.5	0.2	516	4.36×10^{-2}	D_2O	4	-7.2×10^{-7}	298.15	3.0013×10^{8}	624.99	2.14×10^{-5}	1.10×10^{-2}	5.13

3. Cyclic voltammetry

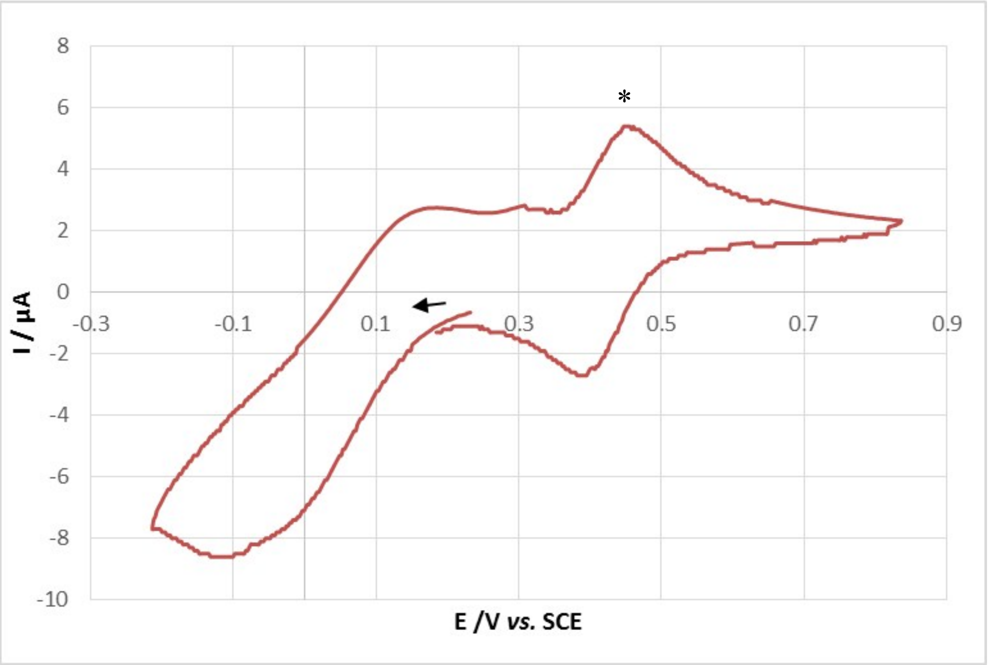


Figure S9. Cyclic voltammogram at 25 °C, initiated by the cathodic sweep, of **4** (concentration of 0.39 mM) in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/NCMe solution at a Pt disk working electrode (*d*=0.5 mm), run at a scan rate of 200 mV s^{-1}. * $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$.

4. pH-metric titration

4.1. Determination of dissociation constants of H$_3$L^{1,2}

Example of the calculation of the dissociation constants of H$_3$L^{1,2} by equations [N.M. Dyatlova, V.Y. Temkina, I.D. Kolpakova, Complexones, Khimiya, Moscow, (1970).]:

$$K_1 = \frac{[\mathrm{H}^+]\{ac_{\mathrm{H_3L}} + [\mathrm{H}^+] - [\mathrm{OH}^-]\}}{(1-\alpha)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]};$$

$$K_2 = \frac{[\mathrm{H}^+]\{(a-1)c_{\mathrm{H_3L}} + [\mathrm{H}^+] - [\mathrm{OH}^-]\}}{(2-a)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]};$$

$$K_3 = \frac{[\mathrm{H}^+]\{(a-2)c_{\mathrm{H_3L}} + [\mathrm{H}^+] - [\mathrm{OH}^-]\}}{(3-a)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]}$$

where $c_{\mathrm{H_3L}}$ is the total concentration of H$_3$L and *a* is the neutralization point.

We titrated 50 mL $1{\cdot}10^{-3}$ M solution of H$_3$L with $2{\cdot}10^{-2}$ M solution of NaOH.

1) After addition of 0.5 mL $2{\cdot}10^{-2}$ M solution of NaOH to 50 mL $1{\cdot}10^{-3}$ M solution of H$_3$L, we observed that pH 3.95, meaning $[\mathrm{H}^+]=1.12{\cdot}10^{-4}$ M and $[\mathrm{OH}^-]=8.91{\cdot}10^{-11}$ M. Thus, total concentration of NaOH: $0.5\ \mathrm{mL}\ 2{\cdot}10^{-2}\ \mathrm{M} = 50.5\ \mathrm{mL}\ x_1\ \mathrm{M} \Rightarrow x_1 = \frac{0.5\cdot 1\cdot 10^{-2}}{50.5} = 1.98\cdot 10^{-4}$ M.

Total concentration of H$_3$L: $50\ \mathrm{mL}\ 1{\cdot}10^{-3}\ \mathrm{M} = 50.5\ \mathrm{mL}\ x_2\ \mathrm{M} \Rightarrow x_2 = \frac{50\cdot 1\cdot 10^{-3}}{50.5} = 9.90\cdot 10^{-4}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{1.98\cdot 10^{-4}}{9.90\cdot 10^{-3}} = 0.20$.

$$K_1 = \frac{[\mathrm{H}^+]\{ac_{\mathrm{H_3L}} + [\mathrm{H}^+] - [\mathrm{OH}^-]\}}{(1-\alpha)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]} = \frac{[1.12\cdot 10^{-4}]\{0.2\cdot 1\cdot 10^{-3} + 1.12\cdot 10^{-4} - 8.91\cdot 10^{-11}\}}{(1-0.2)\cdot 1\cdot 10^{-3} - 1.12\cdot 10^{-4} + 8.91\cdot 10^{-11}} = 5.07\cdot 10^{-5}$$

M (See Table S1).

2) After addition of 1.0 mL $2{\cdot}10^{-2}$ M solution of NaOH to 50 mL $1{\cdot}10^{-3}$ M solution of H_3L, we observed pH 4.22, meaning that $[\mathrm{H}^+]=6.02{\cdot}10^{-5}$ and $[\mathrm{OH}^-]=1.66{\cdot}10^{-10}$ M. Thus, total concentration of NaOH: 1.0 mL $2{\cdot}10^{-2}$ M = 51.0 mL x_1 M $\Rightarrow x_1 = \frac{1.0\cdot 2\cdot 10^{-2}}{51.0} = 3.92\cdot 10^{-4}$ M.

Total concentration of H_3L: 50 mL $1{\cdot}10^{-3}$ M = 51.0 mL x_2 M $\Rightarrow x_2 = \frac{50\cdot 1\cdot 10^{-3}}{51.0} = 9.80\cdot 10^{-4}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{3.92\cdot 10^{-4}}{9.80\cdot 10^{-4}} = 0.40$.

$$K_1 = \frac{[\mathrm{H}^+]\{ac_{\mathrm{H_3L}} + [\mathrm{H}^+] - [\mathrm{OH}^-]\}}{(1-\alpha)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]} = \frac{[6.02\cdot 10^{-5}]\{0.4\cdot 1\cdot 10^{-3} + 6.02\cdot 10^{-5} - 1.66\cdot 10^{-10}\}}{(1-0.4)\cdot 1\cdot 10^{-3} - 6.02\cdot 10^{-5} + 1.66\cdot 10^{-10}} = 5.12\cdot 10^{-5}$$

M (See Table S2).

3) After addition of 1.5 mL $2{\cdot}10^{-2}$ M solution of NaOH to 50 mL $1{\cdot}10^{-3}$ M solution of H_3L, we observed pH 4.49, meaning that $[\mathrm{H}^+]=3.23{\cdot}10^{-5}$ and $[\mathrm{OH}^-]=3.09{\cdot}10^{-10}$ M. Thus, total concentration of NaOH: 1.5 mL $2{\cdot}10^{-2}$ M = 51.5 mL x_1 M $\Rightarrow x_1 = \frac{1.5\cdot 2\cdot 10^{-2}}{51.5} = 5.82\cdot 10^{-4}$ M.

Total concentration of H_3L: 50 mL $1{\cdot}10^{-3}$ M = 51.5 mL x_2 M $\Rightarrow x_2 = \frac{50\cdot 1\cdot 10^{-3}}{51.5} = 9.71\cdot 10^{-4}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{5.82\cdot 10^{-4}}{9.71\cdot 10^{-4}} = 0.60$.

$$K_1 = \frac{[\mathrm{H}^+]\{ac_{\mathrm{H_3L}} + [\mathrm{H}^+] - [\mathrm{OH}^-]\}}{(1-\alpha)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]} = \frac{[3.23\cdot 10^{-5}]\{0.6\cdot 1\cdot 10^{-3} + 3.23\cdot 10^{-5} - 3.09\cdot 10^{-10}\}}{(1-0.6)\cdot 1\cdot 10^{-3} - 3.23\cdot 10^{-5} + 3.09\cdot 10^{-10}} = 4.89\cdot 10^{-5}$$

M (See Table S2).

4) etc.

Table S2. Calculation of the dissociation constants of H_3L^1.

V_{KOH}, mL	a	pH	$[\mathrm{H}^+]$, M	$[\mathrm{OH}^-]$, M	K_1, K_2 and K_3, M	pK_1, pK_2 and pK_3
0.5	0.20	3.95	$1.12{\cdot}10^{-4}$	$8.91{\cdot}10^{-11}$	$5.07{\cdot}10^{-5}$	4.30
1.0	0.40	4.22	$6.02{\cdot}10^{-5}$	$1.66{\cdot}10^{-10}$	$5.12{\cdot}10^{-5}$	4.29
1.5	0.60	4.49	$3.23{\cdot}10^{-5}$	$3.09{\cdot}10^{-10}$	$4.89{\cdot}10^{-5}$	4.31
2.0	0.80	4.92	$1.20{\cdot}10^{-5}$	$8.32{\cdot}10^{-10}$	$5.18{\cdot}10^{-5}$	4.29
2.5	1.00	5.54	$2.88{\cdot}10^{-6}$	$3.47{\cdot}10^{-9}$	–	pK_1=4.30±0.01
3.0	1.20	6.18	$6.61{\cdot}10^{-7}$	$1.51{\cdot}10^{-8}$	$1.65{\cdot}10^{-7}$	6.78
3.5	1.40	6.58	$2.63{\cdot}10^{-7}$	$3.80{\cdot}10^{-8}$	$1.75{\cdot}10^{-7}$	6.76
4.0	1.60	6.95	$1.12{\cdot}10^{-7}$	$8.91{\cdot}10^{-8}$	$1.68{\cdot}10^{-7}$	6.78
4.5	1.80	7.36	$4.36{\cdot}10^{-8}$	$2.29{\cdot}10^{-7}$	$1.74{\cdot}10^{-7}$	6.76
5.0	2.00	8.52	$3.02{\cdot}10^{-9}$	$3.31{\cdot}10^{-6}$	–	pK_2=6.77±0.01
5.5	2.20	9.73	$1.86{\cdot}10^{-10}$	$5.37{\cdot}10^{-5}$	$3.19{\cdot}10^{-11}$	10.50
6.0	2.40	10.11	$7.76{\cdot}10^{-11}$	$1.29{\cdot}10^{-4}$	$2.88{\cdot}10^{-11}$	10.54
6.5	2.60	10.32	$4.79{\cdot}10^{-11}$	$2.09{\cdot}10^{-4}$	$3.07{\cdot}10^{-11}$	10.51
7.0	2.80	10.50	$3.16{\cdot}10^{-11}$	$3.16{\cdot}10^{-4}$	$2.96{\cdot}10^{-11}$	10.51
7.5	3.00	10.83	$1.48{\cdot}10^{-11}$	$6.76{\cdot}10^{-4}$	–	pK_3=10.51±0.03

Table S3. Calculation of the dissociation constants of H_3L^2.

V_{KOH}, mL	*a*	pH	$[H^+]$, M	$[OH^-]$, M	K_1, K_2 and K_3, M	pK_1, pK_2 and pK_3
0.5	0.20	7.17	$6.76 \cdot 10^{-8}$	$1.48 \cdot 10^{-7}$	$1.69 \cdot 10^{-8}$	7.77
1.0	0.40	7.55	$2.82 \cdot 10^{-8}$	$3.55 \cdot 10^{-7}$	$1.88 \cdot 10^{-8}$	7.73
1.5	0.60	7.90	$1.26 \cdot 10^{-8}$	$7.94 \cdot 10^{-7}$	$1.89 \cdot 10^{-8}$	7.73
2.0	0.80	8.36	$4.36 \cdot 10^{-9}$	$2.29 \cdot 10^{-6}$	$1.71 \cdot 10^{-8}$	7.77
2.5	1.00	8.75	$1.79 \cdot 10^{-9}$	$5.62 \cdot 10^{-6}$	–	pK_1=7.75±0.02
3.0	1.20	9.11	$7.76 \cdot 10^{-10}$	$1.29 \cdot 10^{-5}$	$1.79 \cdot 10^{-10}$	9.75
3.5	1.40	9.47	$3.39 \cdot 10^{-10}$	$2.95 \cdot 10^{-5}$	$1.99 \cdot 10^{-10}$	9.70
4.0	1.60	9.77	$1.70 \cdot 10^{-10}$	$5.89 \cdot 10^{-5}$	$2.00 \cdot 10^{-10}$	9.70
4.5	1.80	10.01	$9.77 \cdot 10^{-11}$	$1.02 \cdot 10^{-4}$	$2.25 \cdot 10^{-10}$	10.65
5.0	2.00	10.04	$9.12 \cdot 10^{-11}$	$1.10 \cdot 10^{-5}$	–	pK_2=9.70±0.05
5.5	2.20	10.08	$8.32 \cdot 10^{-11}$	$1.20 \cdot 10^{-4}$	$7.23 \cdot 10^{-12}$	11.14
6.0	2.40	10.39	$4.07 \cdot 10^{-11}$	$2.45 \cdot 10^{-4}$	$7.46 \cdot 10^{-12}$	11.13
6.5	2.60	10.58	$2.63 \cdot 10^{-11}$	$3.80 \cdot 10^{-4}$	$7.42 \cdot 10^{-12}$	11.13
7.0	2.80	10.71	$1.95 \cdot 10^{-11}$	$5.13 \cdot 10^{-4}$	$7.84 \cdot 10^{-12}$	11.11
7.5	3.00	10.96	$1.09 \cdot 10^{-11}$	$9.02 \cdot 10^{-4}$	–	pK_3=11.13±0.02

4.2. Determination of stability constant of 1−4

To determine the stability constant, the following relationships were used [a) J. Inczédy, Analytical Application of Complex Equilibria, Budapest: Akademiai Kiado, **1976**; b) S. Chaberak, A. A. Martell, *J. Am. Chem. Soc.* **1952**, *74*, 5052]:

$$[L^{3-}] = \frac{(3-a)c_{H_3L} - [H^+] + [OH^-]}{[H^+]K_1^1 + 2[H^+]^2 K_1^1 K_2^1 + 3[H^+]^3 K_1^1 K_2^1 K_3^1},$$

$$\alpha_{L(H)} = 1 + [H^+]K_1^1 + [H^+]^2 K_1^1 K_2^1 + [H^+]^3 K_1^1 K_2^1 K_3^1,$$

$$\beta = \frac{c_{H_3L} - [L^{3-}]\alpha_{L(H)}}{[L^{3-}]^2 \alpha_{L(H)}}$$

where $c_{Me} = 1.00 \times 10^{-3}$ M, $c_{H_3L} = 1.00 \times 10^{-3}$ M, $c_{MeOH} = 1.00 \times 10^{-3}$ M K_1^1, K_2^1 and K_3^1 are the protonation constants of L^{3-}, HL^{2-} and H_2L^- ($K_1^1 = 1/K_3$, $K_2^1 = 1/K_2$ and $K_3^1 = 1/K_1$) and *a* is the neutralization point.

Dissociation constants of H_3L^1:

$$pK_1 = 4.30 \Rightarrow K_1 = 5.02 \cdot 10^{-5}\text{ M},\ pK_2 = 6.77 \Rightarrow K_2 = 1.70 \cdot 10^{-7}\text{ M}$$
$$\text{and } pK_3 = 10.51 \Rightarrow K_3 = 3.09 \cdot 10^{-11}\text{ M}.$$

Protonation constants:

$K_1^1 = 1/K_3 = 1/3.09 \cdot 10^{-11} = 3.24 \cdot 10^{10}$ M^{-1}, $K_2^1 = 1/K_2 = 1/1.70 \cdot 10^{-7} = 5.88 \cdot 10^{6}$ M^{-1} and $K_3^1 = 1/K_1 = 1/5.02 \cdot 10^{-5} = 1.99 \cdot 10^{4}$ M^{-1}.

We titrated 50.0 mL of a water solution with $1.00 \cdot 10^{-3}$ M of H_3L^1, $1.00 \cdot 10^{-3}$ M of MeOH and $1.00 \cdot 10^{-3}$ M of Cu^{2+}, with a $2.00 \cdot 10^{-2}$ M solution of NaOH.

i) After addition of 1.00 mL of $2.00 \cdot 10^{-2}$ M solution of NaOH to 50.0 mL of $1.00 \cdot 10^{-3}$ M solution of Cu^{2+}+H_3L^1, we observed that pH 3.48 ⇒ $[H^+] = 3.31 \cdot 10^{-4}$ and $[OH^-] = 3.02 \cdot 10^{-11}$ M.

Total concentration of NaOH:

1.00 mL $2.00 \cdot 10^{-2}$ M = 51.0 mL x_1 M ⇒ $x_1 = 3.92 \cdot 10^{-4}$ M.

Total concentration of Cu^{2+}+H_3L^1:

50.0 mL $1.00 \cdot 10^{-3}$ M = 51.0 mL x_2 M ⇒ $x_2 = 9.80 \cdot 10^{-4}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{3.92 \cdot 10^{-4}}{9.80 \cdot 10^{-4}} = 0.40$

$$[\mathrm{L}^{3-}] = \frac{(3-a)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]}{[\mathrm{H}^+]K_1^1 + 2[\mathrm{H}^+]^2 K_1^1 K_2^1 + 3[\mathrm{H}^+]^3 K_1^1 K_2^1 K_3^1} =$$

$$= \frac{(3-0.4)\cdot 1\cdot 10^{-3} - 3.31\cdot 10^{-4} + 3.02\cdot 10^{-11}}{3.31\cdot 10^{-4}\cdot 3.24\cdot 10^{10} + 2(3.31\cdot 10^{-4})^2 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6} + 3(3.31\cdot 10^{-4})^3 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6}\cdot 1.99\cdot 10^{4}} = 5.00\cdot 10^{-15}\,\mathrm{M}$$

$$\alpha_{L(H)} = 1 + [\mathrm{H}^+]K_1^1 + [\mathrm{H}^+]^2 K_1^1 K_2^1 + [\mathrm{H}^+]^3 K_1^1 K_2^1 K_3^1 =$$

$$= 1 + 3.31\cdot 10^{-4}\cdot 3.24\cdot 10^{10} + (3.31\cdot 10^{-4})^2 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6} + (3.31\cdot 10^{-4})^3 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6}\cdot 1.99\cdot 10^{4} = 1.57\cdot 10^{11}$$

$$\beta = \frac{c_{\mathrm{H_3L}} - [\mathrm{L}^{3-}]\alpha_{\mathrm{L(H)}}}{[\mathrm{L}^{3-}]^2\alpha_{\mathrm{L(H)}}} = \frac{1.00\cdot 10^{-3} - 5.00\cdot 10^{-15}\cdot 1.57\cdot 10^{11}}{(5.00\cdot 10^{-15})^2\cdot 1.57\cdot 10^{11}} = 5.48\cdot 10^{13} \Rightarrow \lg\beta = 13.74.$$

(See Table S4).

ii) After addition of 2.00 mL of $2.00\cdot 10^{-2}$ M solution of NaOH to 50.0 mL of $1.00\cdot 10^{-3}$ M solution of $\mathrm{Cu^{2+}+H_3L^1}$ and $1.00\cdot 10^{-3}$ M of MeOH we observed that pH 4.73 $\Rightarrow [\mathrm{H^+}] = 1.86\cdot 10^{-5}$ and $[\mathrm{OH^-}] = 5.37\cdot 10^{-10}$ M.

Total concentration of NaOH:

2.00 mL $2.00\cdot 10^{-2}$ M = 52.0 mL x_1 M $\Rightarrow x_1 = 7.69\cdot 10^{-4}$ M.

Total concentration of $\mathrm{Cu^{2+}+H_3L^1}$:

50.0 mL $1.00\cdot 10^{-3}$ M = 52.0 mL x_2 M $\Rightarrow x_2 = 9.61\cdot 10^{-4}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{7.69\cdot 10^{-4}}{9.61\cdot 10^{-4}} = 0.80$

$$[\mathrm{L}^{3-}] = \frac{(3-a)c_{\mathrm{H_3L}} - [\mathrm{H}^+] + [\mathrm{OH}^-]}{[\mathrm{H}^+]K_1^1 + 2[\mathrm{H}^+]^2 K_1^1 K_2^1 + 3[\mathrm{H}^+]^3 K_1^1 K_2^1 K_3^1} =$$

$$= \frac{(3-0.8)\cdot 1\cdot 10^{-3} - 2.57\cdot 10^{-4} + 3.89\cdot 10^{-11}}{2.57\cdot 10^{-4}\cdot 3.24\cdot 10^{10} + 2(2.57\cdot 10^{-4})^2 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6} + 3(2.57\cdot 10^{-4})^3 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6}\cdot 1.99\cdot 10^{4}} = 8.90\cdot 10^{-15}\,\mathrm{M}$$

$$\alpha_{L(H)} = 1 + [\mathrm{H}^+]K_1^1 + [\mathrm{H}^+]^2 K_1^1 K_2^1 + [\mathrm{H}^+]^3 K_1^1 K_2^1 K_3^1 =$$

$$= 1 + 2.57\cdot 10^{-4}\cdot 3.24\cdot 10^{10} + (2.57\cdot 10^{-4})^2 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6} + (2.57\cdot 10^{-4})^3 3.24\cdot 10^{10}\cdot 5.88\cdot 10^{6}\cdot 1.99\cdot 10^{4} = 7.68\cdot 10^{10}$$

$$\beta = \frac{c_{\mathrm{H_3L}} - [\mathrm{L}^{3-}]\alpha_{\mathrm{L(H)}}}{[\mathrm{L}^{3-}]^2\alpha_{\mathrm{L(H)}}} = \frac{1.00\cdot 10^{-3} - 8.90\cdot 10^{-15}\cdot 7.68\cdot 10^{10}}{(8.90\cdot 10^{-15})^2\cdot 7.68\cdot 10^{10}} = 5.21\cdot 10^{13} \Rightarrow \lg\beta = 13.72.$$

(See Table S4).

iii) etc.

Table S4. Calculation of the stability constant of **1** at 25 °C, in aqueous solution.

V_{NaOH}, mL	a	pH	$[\mathrm{H^+}]$, M	$[\mathrm{OH^-}]$, M	$[\mathrm{L^{3-}}]$, M	$\alpha_{L(H)}$	$\lg\beta$
1.00	0.40	3.48	$3.31\cdot 10^{-4}$	$3.02\cdot 10^{-11}$	$5.00\cdot 10^{-15}$	$1.57\cdot 10^{11}$	13.74
2.00	0.80	3.59	$2.57\cdot 10^{-4}$	$3.89\cdot 10^{-11}$	$8.90\cdot 10^{-15}$	$7.68\cdot 10^{10}$	13.72
3.00	1.20	3.70	$1.99\cdot 10^{-4}$	$5.01\cdot 10^{-11}$	$1.53\cdot 10^{-14}$	$3.74\cdot 10^{10}$	13.69
4.00	1.60	3.81	$1.55\cdot 10^{-4}$	$6.46\cdot 10^{-11}$	$2.39\cdot 10^{-14}$	$1.87\cdot 10^{10}$	13.71
5.00	2.00	3.93	$1.17\cdot 10^{-4}$	$8.51\cdot 10^{-11}$	$3.26\cdot 10^{-14}$	$1.05\cdot 10^{10}$	13.77
6.00	2.40	4.12	$7.59\cdot 10^{-5}$	$1.32\cdot 10^{-10}$	$7.32\cdot 10^{-14}$	$2.75\cdot 10^{9}$	13.74
7.00	2.80	4.81	$1.55\cdot 10^{-5}$	$6.46\cdot 10^{-10}$	–	–	$\lg\beta = 13.73 \pm 0.04$

Table S5. Calculation of the stability constant of **2** at 25 °C, in aqueous solution.*

V_{NaOH}, mL	a	pH	$[H^+]$, M	$[OH^-]$, M	$[L^{3-}]$, M	$\alpha_{L(H)}$	lgβ
1.00	0.40	3.45	$3.55 \cdot 10^{-4}$	$2.82 \cdot 10^{-11}$	$4.03 \cdot 10^{-15}$	$1.93 \cdot 10^{11}$	13.85
2.00	0.80	3.55	$2.82 \cdot 10^{-4}$	$3.55 \cdot 10^{-11}$	$6.71 \cdot 10^{-15}$	$1.00 \cdot 10^{11}$	13.86
3.00	1.20	3.65	$2.24 \cdot 10^{-4}$	$4.47 \cdot 10^{-11}$	$1.07 \cdot 10^{-14}$	$5.21 \cdot 10^{10}$	13.87
4.00	1.60	3.78	$1.66 \cdot 10^{-4}$	$6.03 \cdot 10^{-11}$	$1.97 \cdot 10^{-14}$	$2.25 \cdot 10^{10}$	13.80
5.00	2.00	3.91	$1.23 \cdot 10^{-4}$	$8.13 \cdot 10^{-11}$	$3.27 \cdot 10^{-14}$	$9.92 \cdot 10^{9}$	13.80
6.00	2.40	4.11	$7.76 \cdot 10^{-5}$	$1.29 \cdot 10^{-10}$	$6.89 \cdot 10^{-14}$	$2.91 \cdot 10^{9}$	13.76
7.00	2.80	4.70	$1.99 \cdot 10^{-5}$	$5.01 \cdot 10^{-10}$	–	–	lg$\beta = 13.82 \pm 0.06$

* $c_{Cu} = 1.00 \times 10^{-3}$ M, $c_{H_3L^1} = 1.00 \times 10^{-3}$ M, $c_{DMF} = 1.00 \times 10^{-3}$ M.

Table S6. Calculation of the stability constant of **3** at 25 °C, in aqueous solution.*

V_{NaOH}, mL	a	pH	$[H^+]$, M	$[OH^-]$, M	$[L^{3-}]$, M	$\alpha_{L(H)}$	lgβ
1.00	0.40	3.62	$2.40 \cdot 10^{-4}$	$4.17 \cdot 10^{-11}$	$1.32 \cdot 10^{-14}$	$6.33 \cdot 10^{10}$	13.16
2.00	0.80	3.73	$1.86 \cdot 10^{-4}$	$5.37 \cdot 10^{-11}$	$2.34 \cdot 10^{-14}$	$3.10 \cdot 10^{10}$	13.21
3.00	1.20	3.86	$1.38 \cdot 10^{-4}$	$7.24 \cdot 10^{-11}$	$4.47 \cdot 10^{-14}$	$1.36 \cdot 10^{10}$	13.16
4.00	1.60	3.99	$1.02 \cdot 10^{-4}$	$9.77 \cdot 10^{-11}$	$8.11 \cdot 10^{-14}$	$6.00 \cdot 10^{9}$	13.12
5.00	2.00	4.12	$7.59 \cdot 10^{-5}$	$1.32 \cdot 10^{-10}$	$1.40 \cdot 10^{-13}$	$2.75 \cdot 10^{9}$	13.06
6.00	2.40	4.30	$5.01 \cdot 10^{-5}$	$1.99 \cdot 10^{-10}$	$2.31 \cdot 10^{-13}$	$9.36 \cdot 10^{8}$	13.20
7.00	2.80	5.11	$7.76 \cdot 10^{-5}$	$1.29 \cdot 10^{-10}$	–	–	lg$\beta = 13.15 \pm 0.09$

* $c_{Cu} = 1.00 \times 10^{-3}$ M, $c_{H_3L^1} = 1.00 \times 10^{-3}$ M, $c_{MeOH} = 1.00 \times 10^{-3}$ M, $c_{en} = 2.00 \times 10^{-3}$ M.

Table S7. Calculation of the stability constant of **4** at 25 °C, in aqueous solution.*

V_{NaOH}, mL	a	pH	$[H^+]$, M	$[OH^-]$, M	$[L^{3-}]$, M	$\alpha_{L(H)}$	lgβ
1.00	0.40	4.35	$4.47 \cdot 10^{-5}$	$2.24 \cdot 10^{-10}$	$2.51 \cdot 10^{-19}$	$3.40 \cdot 10^{15}$	17.84
2.00	0.80	4.48	$3.31 \cdot 10^{-5}$	$3.02 \cdot 10^{-10}$	$5.23 \cdot 10^{-19}$	$1.38 \cdot 10^{15}$	17.87
3.00	1.20	4.59	$2.57 \cdot 10^{-5}$	$3.89 \cdot 10^{-10}$	$9.14 \cdot 10^{-19}$	$6.47 \cdot 10^{14}$	17.88
4.00	1.60	4.72	$1.90 \cdot 10^{-5}$	$5.25 \cdot 10^{-10}$	$1.79 \cdot 10^{-18}$	$2.61 \cdot 10^{14}$	17.80
5.00	2.00	4.84	$1.44 \cdot 10^{-5}$	$6.92 \cdot 10^{-10}$	$2.89 \cdot 10^{-18}$	$1.14 \cdot 10^{14}$	17.85
6.00	2.40	5.02	$9.55 \cdot 10^{-6}$	$1.05 \cdot 10^{-9}$	$5.92 \cdot 10^{-18}$	$3.32 \cdot 10^{13}$	17.84
7.00	2.80	5.81	$1.55 \cdot 10^{-6}$	$6.46 \cdot 10^{-9}$	–	–	lg$\beta = 17.85 \pm 0.05$

* $c_{Fe} = 5.00 \times 10^{-4}$ M, $c_{H_3L^2} = 1.00 \times 10^{-3}$ M. Dissociation constants of H_3L^2: $pK_1 = 7.75 \Rightarrow K_1 = 1.78 \cdot 10^{-8}$ M, $pK_2 = 9.70 \Rightarrow K_2 = 1.99 \cdot 10^{-10}$ M and $pK_3 = 11.13 \Rightarrow K_3 = 7.41 \cdot 10^{-12}$ M.

Protonation constants: $K_1^1 = 1/K_3 = 1/7.41 \cdot 10^{-12} = 1.35 \cdot 10^{11}$ M^{-1}, $K_2^1 = 1/K_2 = 1/1.99 \cdot 10^{-10} = 5.02 \cdot 10^{9}$ M^{-1} and $K_3^1 = 1/K_1 = 1/1.78 \cdot 10^{-8} = 5.62 \cdot 10^{7}$ M^{-1}.

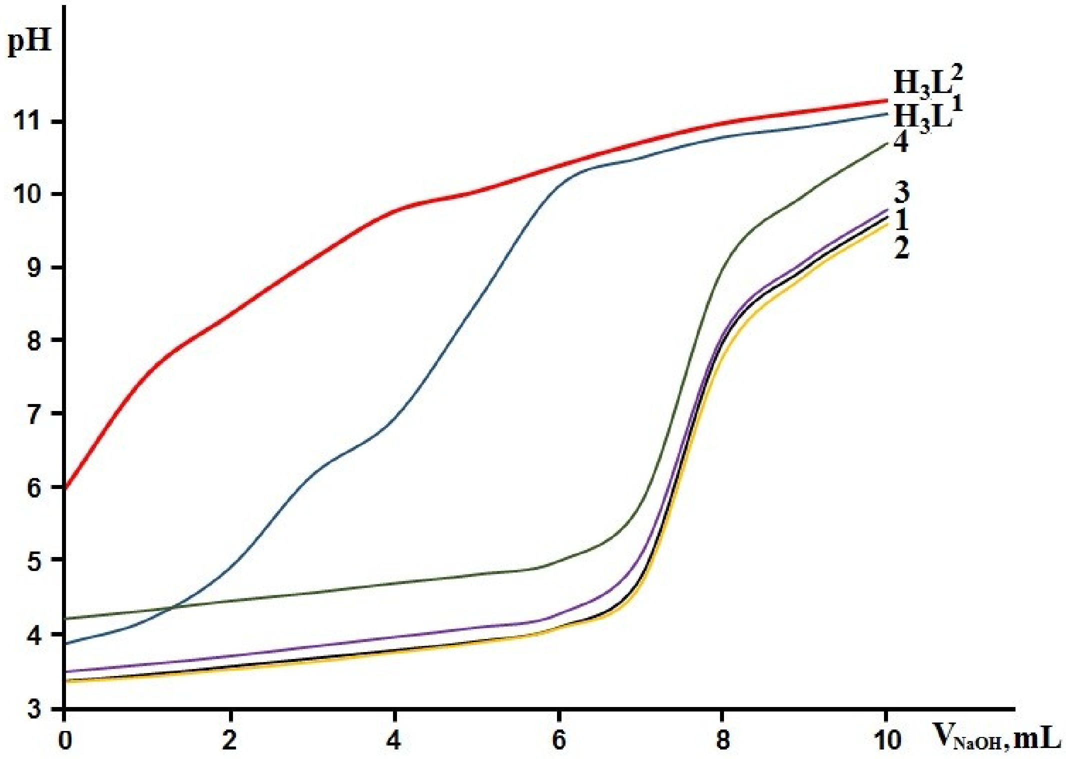


Figure S10. pH-metric titration of $H_3L^{1,2}$ and **1−4**.

5. X-ray data of compounds 1−4

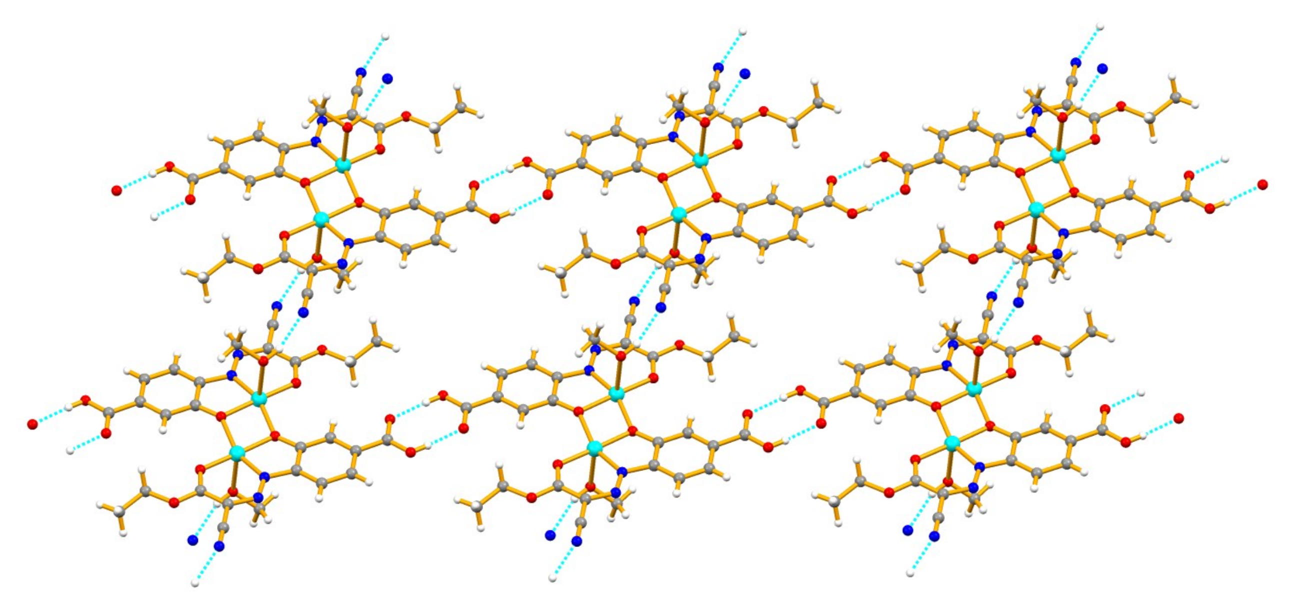
Table S8. Crystal data, experimental parameters and selected details of the refinement calculations of compounds **1**−**4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{26}H_{26}Cu_2N_6O_{12}$	$C_{15}H_{16}CuN_4O_6$	$C_{17}H_{31}CuN_7O_7$	$C_{12}H_7FeN_{22}$
Formula weight	741.61	411.86	509.03	515.25
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	P -1	P -1	C 2/c	P 2_1/n
a (Å)	7.5555(2)	8.3116(5)	30.610(3)	13.9488(13)
b (Å)	9.9153(3)	10.4327(8)	6.9300(6)	9.8504(10)
c (Å)	11.7151(3)	10.7676(8)	23.4642(19)	15.1432(15)
α (deg)	102.312(2)	105.623(4)	90	90
β (deg)	108.492(3)	92.203(4)	103.391(3)	112.754(3)
γ (deg)	102.900(3)	109.315(3)	90	90
Z	1	2	8	4
V (Å3)	772.07(4)	840.18(11)	4842.1(7)	1918.8(3)
ρ_{calc} (Mg/m^3)	1.595	1.628	1.397	1.784
μ(Mo Kα) (mm^{-1})	1.448	1.342	0.952	0.847
R1[a] (I ≤ 2σ)	0.0349	0.0494	0.0412	0.0592
wR2[b] (I I ≤ 2σ)	0.0883	0.1026	0.0866	0.1359
GOF	1.122	1.147	0.999	1.011

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = [\sum[w(Fo^2 - Fc^2)2]/\sum[w(Fo^2)^2]]^{1/2}$.

Table S9. Selected distances (Å) and angles (°) for compounds **1**−**4**.

1		**2**		**3**		**4**	
Cu1–O2	1.9125(18)	Cu1–O2	1.900 (2)	N1–Cu1	2.329(2)	N1–N2	1.305(5)
Cu1–N1	1.920(2)	Cu1–O1	1.911(2)	N21–Cu1	2.005(2)	N1–Fe1	1.874(3)
Cu1–O1	1.9228(17)	Cu1–N1	1.908(3)	N22–Cu1	2.015(2)	N3–N4	1.320(5)
Cu1–O1	1.9486(17)	Cu1–O1	1.938(3)	N31–Cu1	2.011(2)	N3–Fe1	1.939(4)
Cu1–O6	2.335(2)	Cu1–Cu1	2.9669(9)	N32–Cu1	2.012(2)	N6–N7	1.356(5)
Cu1–Cu1	2.9830(6)	O1–C1	1.331(4)	N2–N3	1.298(3)	N8–Fe1	2.000(4)
O1–C1	1.344(3)	O1–Cu1	1.938(3)	C1–N1	1.146(3)	N9–N10	1.365(5)
O1–Cu1	1.9487(17)	O2–C10	1.241(4)	C2–N2	1.347(3)	N12–N13	1.296(5)
O2–C10	1.245(3)	O3–C10	1.313(4)	C3–N3	1.418(3)	N12–Fe1	1.883(3)
O3–C10	1.324(3)	O3–C11	1.454(5)	C4–O3	1.365(3)	N14–N15	1.304(5)
O3–C11	1.460(3)	O4–C7	1.322(5)	C9–O1	1.249(3)	N14–Fe1	1.936(4)
O4–C7	1.240(3)	O5–C7	1.200(5)	C9–O2	1.265(3)	N16–N17	1.363(5)
O5–C7	1.288(3)	O6–C13	1.235(5)	C10–O5	1.230(3)	N18–Fe1	1.961(3)
O6–C13	1.413(5)	N1–N2	1.282(4)	C10–O4	1.344(3)	N22–N21	1.346(6)
N1–N2	1.285(3)	N1–C6	1.412(4)	C11–O4	1.439(3)	N1–Fe1–N12	174.85(15)
N1–C6	1.417(3)	N2–C8	1.343(5)	N21–Cu1–N31	95.29(10)	N1–Fe1–N14	105.00(16)
N2–C8	1.344(3)	N3–C9	1.136(5)	N21–Cu1–N32	178.52(10)	N12–Fe1–N14	79.62(16)
N3–C9	1.132(4)	N4–C13	1.298(6)	N31–Cu1–N32	84.94(9)	N1–Fe1–N3	79.73(15)
O2–Cu1–N1	93.57(8)	N4–C14	1.439(6)	N21–Cu1–N22	84.53(10)	N12–Fe1–N3	102.59(15)
O2–Cu1–O1	175.46(9)	N4–C15	1.441(6)	N31–Cu1–N22	172.78(10)	N14–Fe1–N3	91.97(16)
N1–Cu1–O1	84.50(8)	O2–Cu1–O1	178.71(12)	N32–Cu1–N22	95.06(9)	N1–Fe1–N18	97.18(14)
O2–Cu1–O1	101.38(8)	O2–Cu1–N1	94.56(12)	N21–Cu1–N1	92.93(9)	N12–Fe1–N18	78.21(15)
Cu1–O1–Cu1	100.79(8)	O1–Cu1–N1	84.40(12)	N31–Cu1–N1	93.25(9)	N14–Fe1–N18	157.81(16)
O1–Cu1–O6	102.26(9)	O2–Cu1–O1	101.99(11)	N32–Cu1–N1	88.52(9)	N3–Fe1–N18	92.19(14)
O1–Cu1–O6	94.66(8)	O1–Cu–O1	79.14(12)	N22–Cu1–N1	93.97(9)	N1–Fe1–N8	78.25(15)
O1–Cu1–O1	79.21(8)	N1–Cu1–O1	161.94(13)			N12–Fe1–N8	99.50(15)
N1–Cu1–O1	156.37(9)					N14–Fe1–N8	92.09(16)
						N3–Fe1–N8	157.91(15)
						N18–Fe1–N8	92.20(15)



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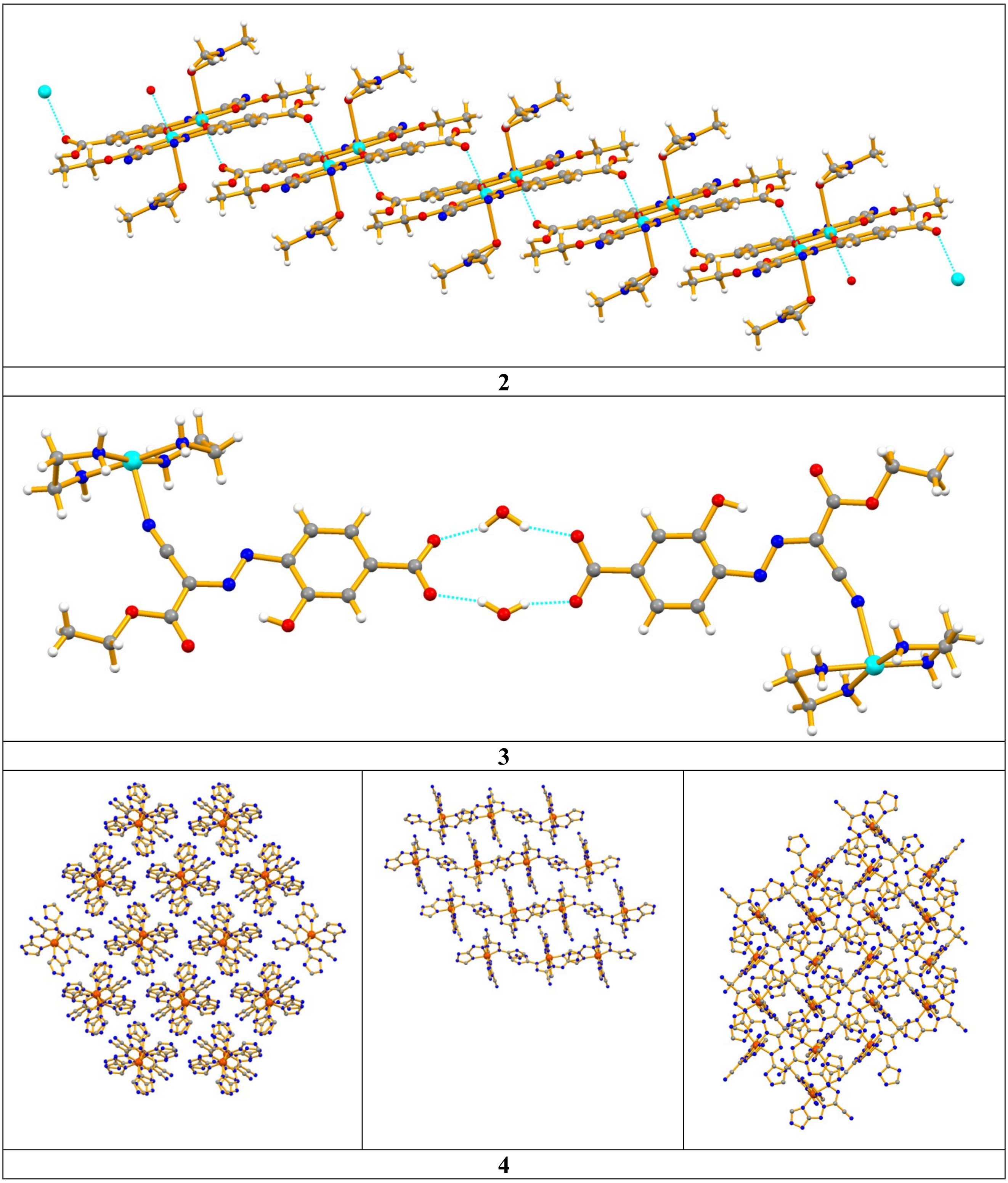

Figure S11. Selected H-bond interactions in **1**–**4** evidencing the 2D network in **1** resulting from the mutual interaction of carboxylic acid groups and the contacts between the hydroxyl group of coordinated methanol with the cyanide N-atom of a neighboring molecules. Packing diagrams for compound **4**, viewed down the crystallographic *a*, *b* and *c* axis (left, centre and right, in this order).

6. Catalytic activity of 1−4

Table S10. MW-assisted solvent-free oxidation of 1-phenylethanol using **1−4** as catalyst precursors.[a]

Entry	Pre-catalyst	Additive (mol % *vs.* substrate)	Reaction temperature /°C	Reaction time /h	Yield[b] /%	TON[c]	TOF[d] /h^{-1}
1	**1**	-	80	0.5	35.3	172.5	345.0
2	**1**	-	100	0.5	82.7	414.4	828.7
3	**1**	-	120	0.25	57.0	293.9	1175.5
4	**1**	-	120	0.5	94.0	471.1	942.3
5	**1**	-	120	1.0	99.9	496.3	496.3
6	**1**	-	120	1.5	87.9	440.7	293.8
7	**1**	TEMPO (2.5)	120	1.0	94.9	489.4	489.4
8	**2**	-	80	0.5	9.9	50.9	101.9
9	**2**	-	100	0.5	36.1	181.4	362.8
10	**2**	-	120	0.25	41.1	188.1	752.2
11	**2**	-	120	0.5	84.6	414.8	829.6
12	**2**	-	120	1.0	93.4	458.1	458.1
13	**2**	-	120	1.5	84.9	416.4	277.6
14	**2**	TEMPO (2.5)	120	1.0	93.8	460.2	460.2
15	**3**	-	80	0.5	30.2	160.4	320.8
16	**3**	-	100	0.5	77.6	396.0	792.0
17	**3**	-	120	0.25	62.5	332.0	1328.2
18	**3**	-	120	0.5	95.0	465.7	931.4
19	**3**	-	120	1.0	99.9	485.5	485.5
20	**3**	-	120	1.5	85.8	420.8	280.5
21	**3**	TEMPO (2.5)	120	1.0	98.7	483.9	483.9
22	**4**	-	80	0.5	9.2	47.3	94.5
23	**4**	-	100	0.5	27.3	135.5	271.1
24	**4**	-	120	0.25	27.4	130.8	523.4
25	**4**	-	120	0.5	44.9	222.9	445.8
26	**4**	-	120	1.0	62.1	308.1	308.1
27	**4**	-	120	1.5	78.5	389.5	259.7
28	**4**		120	2.0	75.0	372.1	186.1
29	**4**		150	1.5	71.0	352.3	234.9
30	**4**	TEMPO (2.5)	120	1.0	65.8	326.5	326.5
31	**-**	-	120	0.5	-	-	
32	**H_3L^1**	-	120	0.5	2.3	11.9	23.8
33	**H_3L^2**	-	120	0.5	-	-	-
34	**1**	$CBrCl_3$ (100)	120	0.5	2.8	14.4	28.8
35	**1**	Ph_2NH (100)	120	0.50	1.5	7.7	15.4
36	**2**	$CBrCl_3$ (100)	120	0.5	3.2	16.1	32.2
37	**2**	Ph_2NH (100)	120	0.5	1.5	7.5	15.0
38	**3**	$CBrCl_3$ (100)	120	0.5	4.2	22.3	44.6
39	**3**	Ph_2NH (100)	120	0.5	-	-	-
40	**4**	$CBrCl_3$ (100)	120	0.5	4.4	22.7	45.4
41	**4**	Ph_2NH (100)	120	0.5	1.6	8.3	16.6

[a]Reaction conditions unless stated otherwise: 2.5 mmol of 1-phenylethanol, 5 µmol (0.2 mol % *vs*. substrate) of **1−4**, 5 mmol of TBHP (2 equiv., 70% in H_2O), 0.5, 1.0, 1.5 and 2.0 h reaction time, 80, 100, 120 and 150 °C reaction temperature, MW irradiation (up to 20 W power). [b]Moles of acetophenone per 100 mol of 1-phenylethanol (GC yield), >99% selectivity. [c]Turnover number = number of moles of product per mol of catalyst precursor. [d]TOF = TON per hour (values in brackets).

Table S11. MW-assisted solvent-free oxidation of benzilic alcohol, cinnamyl alcohol, bezhydrol, cyclooctanol, cyclohexanol, isoborneol and fenchyl alcohol using **1−4** as catalyst precursors.[a]

Entry	Pre-catalyst	Substrate	Yield[b] /%	TON[c]	TOF[d] /h^{-1}
1	**1**	Benzyl alcohol	99.9	148.5	148.5
2	**3**	Benzyl alcohol	99.9	114.5	114.5
3	**1**	Cinnamyl alcohol	6.1	31.3	31.3
4	**3**	Cinnamyl alcohol	4.8	24.1	24.1
5	**1**	Benzhydrol	83.2	417.1	417.1
6	**3**	Benzhydrol	80.1	392.8	392.8
7	**1**	Cyclooctanol	72.9	375.6	375.6
8	**3**	Cyclooctanol	68.0	346.8	346.8
9	**1**	Cyclohexanol	31.6	150.2	150.2
10	**3**	Cyclohexanol	30.3	138.0	138.0
11	**1**	Isoborneol	93.0	478.8	478.8
12	**3**	Isoborneol	94.2	461.9	461.9
13	**1**	Fenchyl alcohol	38.7	199.5	199.5
14	**3**	Fenchyl alcohol	53.4	261.9	261.9
15	**1**	1,2-Cyclohexanediol	51.5 [e]	265.6	265.6
16	**3**	1,2-Cyclohexanediol	56.0 [e]	297.3	297.3
17	**1**	1,4-Cyclohexanediol	18.1 [e]	93.6	93.6
18	**3**	1,4-Cyclohexanediol	23.4 [e]	124.2	124.2

[a] Reaction conditions unless stated otherwise: 2.5 mmol of substrate, 5 µmol (0.2 mol % *vs.* substrate) of **1−4**, 5 mmol of TBHP (2 equiv., 70% in H_2O), 1.0 h reaction time, 120 °C reaction temperature, MW irradiation (up to 20 W power). [b] Moles of aldehyde or ketone per 100 mol of alcohol substrate (GC yield), >99% selectivity. [c] Turnover number = number of moles of product per mol of catalyst precursor. [d] TOF = TON per hour (values in brackets). [e] *ca* 94 % selectivity.